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(54) PROCESSING METHOD OF FIBRE PRODUCTS  
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[Note: All names, addresses, company names, and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified with numeral prefix or general form of plurality suffix. Translator's note]

## **DETAILED EXPLANATION OF THE INVENTION**

This invention relates to a new processing method that provides fibre products with durable water repellent property and (or) oil repellent property as well as antistatic property.

With fast advancement of synthetic fibre in recent years, a processing method that provides water and oil repellent properties, and antistatic property has been desired in the fields of clothing, in particular, sports wear, or coats and the others.

That is to say, synthetic fibre have been known for such defects as an easy generation of static electricity because of their hydrophobicity to easily adsorb dusts in air due to said static electricity, and also to cause trousers or skirts and like to stick to one's body or to generate flickers; and improvement on such defects has been much desired.

In addition, durable water repellent effect is beneficial as it prevents from wetting by water and adhesion of water-soluble dirt; and durable oil repellent effect is effective from the standpoint of prevention from adhesion of oily dirt.

However, above-explained water and oil repellent properties and antistatic property are contrary to each other; and it is very difficult to provide both such properties, and therefore, no such processing method has yet been known. That is to say, when the fibre is treated with water and oil repellents, antistatic property declines, and when antistatic agent is applied to the fibre, water and oil repellent properties show decline. It is not possible to attain the prescribed purpose even when both treatment agents are applied at the same time.

This invention sets out to completely conquer above-explained conflict, and at the same time, it provides durable processing effects. That is to say, this invention's method is characterized by that fact that it allows an easy attainment of effects of water repellency, oil repellency, and antistatic property through 2 stage treatments, in other words, after applying water repellent and (or) oil repellent agents to the fibre products (first stage treatment), they are treated with an antistatic agent that is dissolved or dispersed in solvents or penetrating agents showing affinity to the processing agents used in said first stage treatment (second stage treatment).

According to this invention's method, because solvents or penetrating agents that show affinity with the processing agents used in the first stage treatment are used as a medium of antistatic agent for the second stage treatment, no troubles should occur from the standpoint of compounding; and in addition, it is possible to easily disperse and adhere antistatic agent that is dissolved or dispersed in the solvent showing affinity with said water and oil repellent agents to the layer having said water and oil repellent agents which have been formed on the surface of fibre products beforehand. In addition, although the first stage treatment generally results in generation of much static electricity on the fibre products of post treatment because hydrophobic chemicals are generally used, according to this invention's method, because antistatic agents are applied at the second stage treatment to allow display of the antistatic effect, and generation of static electricity becomes very small. In addition, it is considered that through use of solvent or penetrating agents which show affinity to the water and oil repellent agents that are applied at the first stage treatment, somewhat of physical and chemical bonding may be created among water and oil repellent agents that show hydrophobic property and hydrophobic portion of the antistatic agents during application of said antistatic agent to allow favorable actions with durability such as laundry resistance or dry cleaning resistance, and the like.

Regarding water and oil repellent agents that can be used in this invention's method, for instance, the ones of wax.aluminium salt group, wax.zirconium salt group, quaternary pyridinium group, aliphatic group amide.resin group, silicone group, or fluorine resin group and the like may be used.

In addition regarding antistatic agents, for instance, phosphate group (anion group), quaternary ammonium group (cation group), betaine group (amphoteric group), or polyoxyethylene group (non-ion group) and the like may be used; and as seen in the cation group, use of such agents showing water repellency themselves can provide good effects more easily.

Regarding solvents, dispersants, and penetrating agents showing affinity with water and oil repellent agents, organic solvents or penetrating agents of compounds such as alcohols, ethers, ketones, or benzene group may be appropriately selected and used based on each relationship with chemical structures; and it is preferable to use the ones which show volatile property that easily scatter from the fibre goods after processing and do not remain.

For instance, in the case of water and oil repellent agents of wax.aluminium salt group and wax.zirconium salt group, benzene, chloroform, or ether and the like are appropriate; and in the case of quaternary pyridinium group, ethanol or ether and the like, and in the case of silicone group, benzene and the like, and in the case of fluorine resin group, methanol, or ethanol and the like are appropriate. According to this invention, it is particularly preferable when fluorine resin group water and oil repellent agents are used and methanol or ethanol is used as a solvent.

Regarding the finish processing method of fibre products, after applying said water repellent treatment and (or) oil repellent treatment in accordance to ordinary method (first stage treatment), solution or dispersed solution of antistatic agent may be applied in such manner to preferably provide 0.5 ~ 5% owf through a dip method, spray method, or coating method and the like.

The fibre products that can be subjected to this invention's method include knit or woven cloth of natural fibre such as cotton, wool, linen, or silk and the like, regenerated fibre such as acetate, cupra, viscose, or rayon and the like, synthetic fibre such as polyamide, polyester, polyacrylonitrile, or polypropylene and the like which are processed as alone, mixed fibre spinning, or cross knit and weaving, and nonwoven cloth or paper, and sewn products, coated cloth, or cloth with rubber backing.

The fibre products that are treated by this invention's method are capable of displaying an antistatic capability with excellent durability with absolutely no changes on the water and oil repellent properties to provide products, which are equipped with properties conflicting to each other that cannot be seen on any ordinary products. And therefore, it is a very effective processing method for the fields which require water repellency, oil repellency as well as antistatic property, in particular, outer wears such as rain coats, or jumper coats and the like, knitted suits, and suits for men and women. Examples are shown below.

#### EXAMPLES

Scotchgard FC-208 (Fluorine resin group water and oil repellent made by 3M Co.) and antistatic agents shown in the Table 1 were combined, and they were applied to a polyester-poplin base [cloth] through (1) already known method, in other words, one bath on-stage treatment, and (2) this invention's method, in other words, separate bath two stage treatment and results were compared.

(1) Conventional method	
Scotchgard FC-208	3.5 parts by weight
Hopatex FTN [transliteration] (a stabilizer made by Ciba Co.)	3 parts by weight
isopropanol	40 parts by weight
water	54 parts by weight

A dispersed solution comprising above-explained components to which prescribed amount of each antistatic agent shown in the Table 1 was added, and they were thoroughly stirred to give a treatment solution. Base cloth was dipped in above-explained treatment solution, and after that was squeezed with mangles to give 90% squeezed solution rate, it was air dried, and then, it was heat treated for 3 minutes at 130°C.

(2) This invention's method

Scotchgard FC-208	3.5 parts by weight
Hopatex FTN [transliteration] [a stabilizer made by Ciba Co.)	3 parts by weight
isopropanol	40 parts by weight
water	54 parts by weight

A treatment solution comprising above-explained components was used to dip a base cloth, and after it was squeezed with mangles to give 90% squeezed solution rate, it was air dried, and it was heat treated for 3 minutes at 130°C. Then, antistatic agents which were emulsified and dispersed in water to give prescribed concentration beforehand were dissolved in the solvents shown in the Table 1, and above-explained post-treated base cloth was dipped in this solution, and after it was squeezed and dried to give 90% squeezed solution rate, and it was heat treated for 40 seconds at 150°C.

Results are shown in the Table below.

TABLE 1      PRESCRIPTION

Sample Processing	No.	antistatic agents (maker's name)	application rate (owf)	solvents used (dissolution ratio)
Conventional	1	Permax AW (Yoshimura Yuka)	3	-
Method:	2	Erion A-3 (Sanyo Kasei)	3	-
	3	Neoston 900EP (Gunze Sangyo)	2	-
Method of	1'	Permax AW (Yoshimura Yuka)	3	methanol/water 80/20
Invention	2'	Erion A-3 (Sanyo Kasei)	3	methano/water 80/20

[Note: The antistatic agent shown above are all translated phonetically. Translator's note]

TABLE 2 RESULTS

Sample No.	pre-laundry	water repellency				oil repellency	
		1 x	3 x	5 x	after dry cleaning of 3 times	pre-laundry	after dry cleaning of 3 times
1	80	70-	70-	50+	50-	90	50
2	80-	50+	50-	50	-	80	0
3	70	70+	50+	50	50	100	70
1'	100	100-	100-	90	90+	100	90+
2'	100	100-	100-	90	90+	100	90

(note) Water repellency and oil repellency were judged based on the Scotchgard specification of 3M Co.

TABLE 3 RESULTS

Sample No.	pre-laundry	surface resistance ( $\Omega/\text{cm}^2$ )			
		after laundry	after 3 x of dry cleaning		
		1 x	3 x	5x	
non-treated	$2.0 \times 10^{11}$	-	-	-	-
1	$4.5 \times 10^9$	$5.3 \times 10^{11}$	$3.3 \times 10^{11}$	$3.8 \times 10^{12}$	$6.5 \times 10^{11}$
2	$2.3 \times 10^8$	$1.9 \times 10^{10}$	$4.0 \times 10^{10}$	$5.0 \times 10^{11}$	$7.3 \times 10^{11}$
3	$4.0 \times 10^{11}$	$1.0 \times 10^{12}$	$1.0 \times 10^{12}$	$1.0 \times 10^{12}$	$6.8 \times 10^{11}$
1'	$2.0 \times 10^8$	$3.9 \times 10^9$	$8.2 \times 10^9$	$9.5 \times 10^9$	$5.9 \times 10^9$
2'	$6.0 \times 10^8$	$4.5 \times 10^9$	$4.6 \times 10^9$	$5.9 \times 10^9$	$7.4 \times 10^9$

As it is clear from the results shown in the Table 2 and Table 3, the products by this invention's method show excellent water repellency, oil repellency and antistatic property with durability.

### CLAIMS

- 1 A processing method of fibre products is characterized by the fact that after applying water repellent and (or) oil repellent treatments to fibre products (first stage treatment), they are treated with a solution in which an antistatic agent is dissolved or dispersed in solvent or penetrating agent showing affinity to the treatment agents used in said first state of treatment (second stage treatment).

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## ④繊維製品の加工法

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## 発明の詳細な説明

本発明は繊維製品に耐久性のある撥水性および(又は)撥油性並びに帯電防止性を付与する新規な加工方法に関する。

近年合成繊維の急速な進歩に伴って衣料用分野、殊にスポーツ着、コート類に撥水撥油性と帯電防

止性を兼備した加工法が望まれてきた。

すなわち合成繊維は疎水性のために静電気を発生しやすく、この静電気によつて空気中の塵埃を吸着しやすく、またズボン、スカート類が身体にまつわりつくとか火花を発生するというような欠点があり、その改善が著しく望まれる。

また耐久性のある撥水効果は水による濡れおよび水溶性汚れの付着を防止するために有益であり、耐久性のある撥油効果は油性汚れの付着を防止するために有効である。

しかし上記撥水撥油性と帯電防止性とは性質として相反するものであり、両性質を兼備させることは至難であり、これまでこのような加工法は知られていなかった。すなわち撥水撥油剤で繊維を処理すれば帯電防止性は低下し、また帯電防止剤を繊維に適用すれば撥水撥油性は低下する。両処理剤を同時に適用しても所期の目的を達することができない。

本発明は上述のような矛盾を完全に克服するとともに耐久性のある加工効果を得るものである。すなわち本発明方法は繊維製品に撥水および(又は)撥油加工剤処理(第1段処理)を施して後、該第1段処理に用いた加工剤に親和性のある溶剤

又は浸透剤に帯電防止剤を溶解または分散させた液で処理すること(第2段処理)を特徴とするものであり、2段階処理により容易に撥水、撥油、帯電防止効果を得ることができる。

5 本発明方法では、第1段処理で用いた加工剤と親和性のある溶剤又は浸透剤を第2段処理の帯電防止剤の媒体としているために、配合上のトラブルはなく、また予め繊維製品の表面に形成された撥水撥油剤の層に、該撥水撥油剤に親和性のある溶媒に溶解又は分散された帯電防止剤を容易に均一に分散付着させることができる。また第1段処理は一般に疎水性薬剤を使用するため処理後の繊維品の静電気発生量が多くなるのが普通であるが、本発明方法は第2段処理で帯電防止剤が付与されるので帯電防止効果が発揮され、静電気の発生がきわめて少なくなる。更に、帯電防止剤の適用に際して、第1段処理で施された撥水、撥油剤に親和性のある溶剤又は浸透剤を用いることにより、疎水性を示す撥水、撥油剤と帯電防止剤の疎水性部分とが何らかの物理的、化学的結合をなし、耐洗濯性、耐ドライクリーニング性などの耐久性に有利に作用するものと考えられる。

本発明方法に用いる撥水、撥油剤としては例えばワックス・アルミニウム塩系、ワックス・ジ

25 ルコニウム塩系、第4級ピリジニウム系、脂肪族アマイド・樹脂系、シリコン系、弗素樹脂系のようなものが使用される。

また、帯電防止剤としては、例えばホスフエート系(アニオン系)、第4アンモニウム系(カチオン系)、ベタイン系(両性)、ポリオキシエチレン系(非イオン系)のようなものが使用されるが、カチオン系などに見られるように、それ自身撥水効果のあるものを使用した方がより容易に好結果が得られる。

35 撥水、撥油剤に親和性を有する溶媒、分散媒、浸透剤としてはアルコール類、エーテル類、ケトン類、ペンセン系化合物等の有機溶剤及び浸透剤が適宜その化学構造との関係において選択使用さ

れるが、揮発性を有し、加工後に容易に繊維品から飛散して残存しないものが特に好ましい。

例えばワックス・アルミニウム塩系およびワックス・ジルコニウム塩系の撥水、撥油剤の場合には、ベンゼン、クロロホルム、エーテル等が適当であり、第4級ピリジニウム系の場合にはエタノール、エーテル等、シリコン系の場合にはベンゼン等、弗素樹脂系の場合はメタノール、エタノール等が適当である。本発明では弗素樹脂系撥水撥油剤を用い、溶剤としてメタノール、エタノールを用いるのが特に好ましい。

繊維製品の仕上加工の方法は、通常の方法に従い前記撥水及び(又は)、撥油剤処理(第1段処理)を繊維製品に施したのち、帯電防止剤の溶液又は分散液を浸漬法、スプレー法、コーティング法などにより、好ましくは0.5~5% owf になるよう付与するものである。

本発明方法の対象となる繊維製品には綿、羊毛、麻、絹などの天然繊維、アセテート、キュプラ、ビスコース・レーヨンなどの再生繊維、ポリアミド、ポリエステル、ポリアクリロニトリル、ポリプロピレンなどの合成繊維を単独、混紡、交編織した編織布、不織布紙および縫製加工品、コーティング布、ゴム張布などが含まれる。

本発明方法により処理された繊維製品は撥水、撥油性には何等の変化がなく、かつ耐久性のある優れた帯電防止能を発揮することができ、従来のいかなるものにも見られない相反する特性を兼ね備えた製品が得られる。したがって特に撥水、撥油性と帯電防止性の要求のある分野、レインコート、ジャンパーコートなどの外衣、ニットスーツ、紳士、婦人用スーツ地などのスーツ類にはきわめて有効な加工法である。次に実施例を示す。

#### ※実施例

ポリエステル・ポブリン地に対して、スコッチガードFC-208(3M社製弗素樹脂系撥水撥油剤)と第1表に記載の帯電防止剤を組合わせ、

(1)従来公知の方法、すなわち同浴一段処理と(2)本発明の方法、すなわち別浴二段処理を行ない、その結果を比較検討した。

#### (1) 従来法

スコッチガードFC-208	3.5重量部
ホボテックスFTN (チバ社製安定剤)	3 "
イソプロパノール	40 "
水	54 "

から成る分散液に第1表の各帯電防止剤の所要量を添加し、充分攪拌し、処理液とした。上記処理液に生地を浸漬し、マングルで絞液率が90%になるように絞液した後風乾し、130℃で3分間熱処理した。

#### (2) 本発明法

スコッチガードFC-208	3.5重量部
ホボテックスFTN (チバ社製安定剤)	3 "
イソプロパノール	40 "
水	54 "

からなる処理液に生地を浸漬し、マングルで絞液率が90%になるように絞液した後、風乾し、130℃で3分間熱処理した。次に、予め水で乳化分散した所要濃度の帯電防止剤を第1表に記載の溶剤に溶解し、この液に上記処理生地を浸漬し、絞液率が90%になるように絞液し、乾燥後150℃で40秒間熱処理した。

結果は次表のとおりである。

第 1 表

処 方

加工法	試料 №	帯電防止剤名(メーカー名)	使用量 (owf)	使用溶剤名(容量比)
従 来 法	1	パーマックスAW (吉村油化)	3	_____
	2	エリオンA-3 (三洋化成)	3	_____
	3	ネオアストン900EP (群是産業)	2	_____
本発明法	1'	パーマックスAW (吉村油化)	3	メタノール/水 80/20
	2'	エリオンA-3 (三洋化成)	3	メタノール/水 80/20



第 2 表

結 果

試 料 №	撥 水 性					撥 油 性	
	洗 滌 前	洗 濯 後			ドライクリ ーニング 3 回 後	洗 滌 前	ドライクリ ーニング 3 回 後
		1 回	3 回	5 回			
1	80	70-	70-	50+	50-	90	50
2	80-	50+	50-	50	-	80	0
3	70	70+	50+	50	50	100	70
1'	100	100-	100-	90	90+	100	90+
2'	100	100-	100-	90	90+	100	90

(注) 撥水性、撥油性は3M社のスコッチガード規格により判定

第 3 表

結 果

試 料 №	表 面 抵 抗 ( $\Omega/cm^2$ )				
	洗 滌 前	洗 濯 後			ドライクリ ーニング 3 回 後
		1 回	3 回	5 回	
未 処 理	$2.0 \times 10^{11}$	—	—	—	—
1	$4.5 \times 10^9$	$5.3 \times 10^{11}$	$3.3 \times 10^{11}$	$3.8 \times 10^{12}$	$6.5 \times 10^{11}$
2	$2.3 \times 10^8$	$1.9 \times 10^{10}$	$4.0 \times 10^{10}$	$5.0 \times 10^{11}$	$7.3 \times 10^{11}$
3	$4.0 \times 10^{11}$	$1.0 \times 10^{12}$	$1.0 \times 10^{12}$	$1.0 \times 10^{12}$	$6.8 \times 10^{11}$
1'	$2.0 \times 10^8$	$3.9 \times 10^9$	$8.2 \times 10^9$	$9.5 \times 10^9$	$5.9 \times 10^9$
2'	$6.0 \times 10^8$	$4.5 \times 10^9$	$4.6 \times 10^9$	$5.9 \times 10^9$	$7.4 \times 10^9$

第2表及び第3表の結果から明らかなように本  
発明の方法による製品は耐久性のある優れた撥水、  
撥油、帯電防止性を示す。

特許請求の範囲

1 繊維製品に撥水および(又は)撥油加工剤処

理(第1段処理)を施して後、該第1段処理に用  
いた加工剤に親和性のある溶剤又は浸透剤に帯電

防止剤を溶解または分散させた液で処理すること  
(第2段処理)を特徴とする繊維製品の加工法。